

COORDINATION COMPOUNDS OF SOME
POLYDENTATE CYCLIC AMINES

I. TRIDENTATE AMINES

II. BIDENTATE AMINES

BY

ERROL BATHURST MIDDLETON

A. B., University of Illinois, 1919

M. S., University of Illinois, 1921

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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OF ILLINOIS, 1938

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I

TRIDENTATE AMINES

Considerable work has been done on the rotary power of optically active complexes and the factors which might influence it, but no one has investigated the effect of the valence of the central atom in a complex compound on its rotary power. The essential conditions for such a study are: the metal must have more than one valence, form the same type of resolvable compound in each valence state and not be too highly colored. Several metals were considered for this investigation such as chromium, arsenic, iron, palladium, iridium, ruthenium and platinum.

Mann^{1,2} prepared bistriaminopropane platinous iodide $[\text{Pt}(\text{—CH}_2\text{.NH}_2\text{.CH.NH}_2\text{.CH}_2\text{.NH}_2)_2]\text{I}_2$, a compound in which bivalent platinum has a coordination number of six. Since tetravalent platinum has a characteristic coordination number of six, this points to platinum as the metal best suited to meet these requirements. Mann and Pope³ found bistriaminopropane platinous iodide to be optically inactive.

This work suggested the possibility of trying some other tridentate amine which might possibly form optically active metallic complexes or compounds resolvable into optically active forms. The base selected for this purpose was 1-methyl-2,4,6-triaminocyclohexane, a tridentate base capable of existing in four optically active isomers. This compound is a new base, and was prepared by the catalytic reduction of symmetrical trinitrotoluene.

The platinic complex of 1-methyl-2,4,6-triaminocyclohexane was prepared by the action of anhydrous platinic chloride on the base. The complex, a yellowish solid, was found to be too unstable to resolve, so the preparation of the platinous salt was not attempted.

Further studies with 1-methyl-2,4,6-triaminocyclohexane showed that the most stable metallic complexes were those of cadmium, bivalent mercury and bivalent copper. The composition of these is represented by the general formula $[\text{Me (tachn)} \text{X}_2]$. Alcohol and acetone were used as solvents in the preparation of these complexes.

These complexes are yellowish colored solids, unstable in water and non ionic in character.

Goldschmidt⁴ states that only one amino group in 2,4,6-triaminotoluene is functionally capable of neutralizing the residual affinity of a metal, and Hein and Wagner⁵ working on this assumption prepared a series of metallic complexes of this amine. Their results showed that this was not rigidly true. They obtained, for example, the compound $[\text{Cd (tat)} \text{Cl}_2]$ and the structure assigned by them to this compound showed that two of the amino groups were functionally capable of coordinating with metallic ions, so it can reasonably be assumed that at least two of the amino groups in 1-methyl-2,4,6-triaminocyclohexane can be coordinated in a like manner. Since the carbon atoms in cyclohexane rings do not lie in a plane, this molecule is strainless and all three amino groups in the compound might be coordinated with a metal.

The corresponding metallic complexes of 1-methyl-2,4,6-triaminocyclohexane are much less stable than those of triaminotoluene prepared by Hein and Wagner.⁶

PART II

BIDENTATE CYCLIC AMINES

The results of the study of the metallic complexes of 1-methyl-2,4,6-triaminocyclohexane, and the work of Hein and Wagner⁶ on the coordination compounds of 2,4,6-triaminotoluene suggested the investigation of the composition, properties and stabilities of the bidentate cyclic amines. The particular amines chosen were: the 2,3; 2,4 and the 3,4 diaminotoluenes; the ortho, meta and para phenyldiamines; 2,2'-diamino biphenyl and 1-methyl-2,4-diaminocyclohexane. The 1-methyl-2,4-diaminocyclohexane is a new organic base, and was prepared by the catalytic reduction of 2,4-diamino

toluene. The following metallic salts were used: cupric chloride, cobaltous chloride, mercuric chloride, cadmium chloride and bromide, zinc chloride and nickel bromide. Metallic complexes of the toluenediamines and the ortho, meta and para phenylene diamines were studied in order to find the effects of the introduction of the methyl group on the benzene ring and the position of the amino groups, on the properties and stabilities of the complexes. The phenylene diamine complexes are more stable as a class than the toluenediamines. The complexes of 2,3-diaminotoluene are more stable than those of 2,4-diaminotoluene. Those of 3,4-diaminotoluene are the least stable of the toluenediamine complexes studied. The metallic complexes of 1-methyl-2,4-diaminocyclohexane are less stable than those of 2,4-diaminotoluene.

The investigations of Kharasch and Flenner,⁷ and Kharasch and Marker⁸ on electronegativity have shown that the tolyl group is more electronegative than the phenyl group. Consequently the phenylene diamines are more basic than the toluene diamines, and since the phenylene diamine complexes proved to be more stable than the toluene diamines, it is possible that the more basic a bidentate amine is, the more firmly it is coordinated to the metal.

In an effort to find out which amino group in the polydentate amines is more effective in neutralizing the residual affinity of the metal, a series of cobaltous chloride and cadmium bromide complexes of the ortho-, meta- and para toluidines were prepared. It was found however, that cobaltous chloride reacts with all of the toluidines in the same manner, and with the same speed. There is no appreciable difference in their stabilities toward water. They have the same color, crystalline form and solubility. The cadmium bromide complexes are likewise very similar to each other.

All of the complexes of the bidentate cyclic amines are non ionic in nature, as indicated by the slow precipitation of the halogens in their complexes, with silver nitrate.

A series of metallic complexes of the bi-cyclic amine, 2,2'-diamino biphenyl were prepared for purposes of comparison with those containing one benzene ring only and were found to be

much more stable than those of the phenylenediamines, the toluene-diamines and 1-methyl-2,4-diaminocyclohexane. Their composition is shown by the general formula $[\text{Me}(\text{diphen})_2\text{X}_2]$. No complexes containing one mol of the 2,2'-diamino biphenyl could be prepared. Complexes of the phenylene diamines could be prepared with one or two mols of the amine per mol of salt; for example $[\text{Me}(\text{phen})\text{X}_2]$ and $[\text{Me}(\text{phen})_2\text{X}_2]$. The only complexes of the toluenediamines that could be prepared were those containing one mol of the base coordinated with the metal as $[\text{Me}(\text{dat})\text{X}_2]$.

Hieber and Ries⁹ state that they were able to prepare metallic complexes of ortho-phenylenediamine containing as high as six mols of the diamine per mol of salt, but with the methods of preparation used in this investigation no more than two mols of the base could be made to coordinate with the metal.

A most interesting series of cobaltic complexes containing 2,2'-diaminobiphenyl were prepared. The complex diethylenediamine 2,2'-diaminobiphenyl cobalti chloride, $[\text{Co en}_2(\text{diphen})]\text{Cl}_3$ were prepared as a stable orange compound by the action on 2,2'-diaminobiphenyl on di ethylenediamine cobalti chloride. The compound di chloro di 2,2'-diaminobiphenyl cobalti chloride was prepared by the oxidation of a mixture of cobaltous chloride and 2,2'-diaminobiphenyl with air and hydrogen peroxide. It is a green, crystalline compound. Very good evidence points to the existence of the orange yellow compound $[\text{CO}(\text{diphen})_3]\text{Cl}_3$, prepared by the oxidation of a mixture of cobaltous chloride and 2,2'-diaminobiphenyl with chlorine. The compound is stable only when air is excluded.

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ABBREVIATIONS

tachn—1-methyl 2,4,6-triaminocyclohexane

X—halogens

dat—diaminotoluene

diphen—2,2'diaminobiphenyl

en—ethylenediamine

Me—metal

phen—phenylenediamine

tachn—1-methyl 2,4,6-triaminocyclohexane

VITA

The writer was born in Decatur, Illinois, on January 23, 1898. He received his elementary education in Illinois and Texas, and was graduated from high school in Eagle Lake, Texas, in June, 1914. His undergraduate work was done at Rice Institute, and the University of Illinois. He received his Bachelor of Arts degree in 1919 from the University of Illinois, and his Master of Science degree in 1921, from the same school. He held an assistantship in chemistry while attending the University of Illinois from 1919-21. He taught in the science department of the Patti Welder High School, Victoria, Texas, in 1921-22 and in the chemistry department of the Agricultural and Mechanical College of Texas in 1922-23. During the next three years he was employed as a chemist in the cottonseed oil and petroleum industries in Texas. He returned to the Agricultural and Mechanical College of Texas in 1926. He has been on the teaching staff of the same college since that time, and holds the rank of assistant professor of chemistry.

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